Reply to Comment on "Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni_4"

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Abstract

Here we respond briefly to a comment on our work in arXiv:cond-mat/0405501.

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A recent Comment [1] was posted on cond-mat on our paper entitled "Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni_4" [2]. The main points of this comment can be summarized as follows:

1) That our paper reported experimental studies on the $S = 4$ single molecule magnet Ni_4 using a method that combines high sensitivity magnetic measurements with microwave spectroscopy, which was similar to the work posted on cond-mat a few weeks earlier on the $S = 1/2$ molecule V_{15} [3]. The implication was that this early posting gives Wernsdorfer claim to being the 'originator' of this magnetic measurement method.

2) That pulsed-radiation relaxation experiments, like those we present, do not give directly the spin-lattice relaxation time T_1 but the spin-phonon-bottleneck time. As a consequence our finding of an increase of T_1 with frequency is not contrary to general ideas.

3) The final claim is that "... all statements concerning the observation of quantum coherence" have not yet demonstrated.

We address these points in the order above.

First, we started planning and discussing these experiments three years ago, including ordering the necessary equipment [4]. The experiments on Ni_4 were conducted over the last six months. The cited work was presented in an invited talk [5] at the APS March Meeting and at an earlier conference [6]. Our paper was submitted to Science after the March Meeting (on April 9^{th} 2004, one week before ref. [3]) and shortly thereafter to Physical Review Letters. We also note that while our paper was under consideration for publication, an interesting related work by Bal et al. [7] appeared. The timing of these publications and talks makes it clear that these papers correspond to independent research carried out in *parallel*. These experiments and other earlier publications reflect the continued and growing interest of the community in coherent quantum phenomena in SMMs [8, 9]. The ideas of such combined magnetic/microwave experiments were actively discussed by many in the SMM community [4, 10, 11], and similar experiments were published some time ago, which investigated quantum superposition states in superconducting quantum interference devices [12, 13].

In our experiments high sensitivity Hall magnetometry was combined with microwave spectroscopy. We note that Hall magnetometers have recently been demonstrated to have sensitivities of 5×10^5 spins [14] and higher spin sensitivities are certainly possible, with material and device improvements. There is also no fundamental reason that Hall magne-

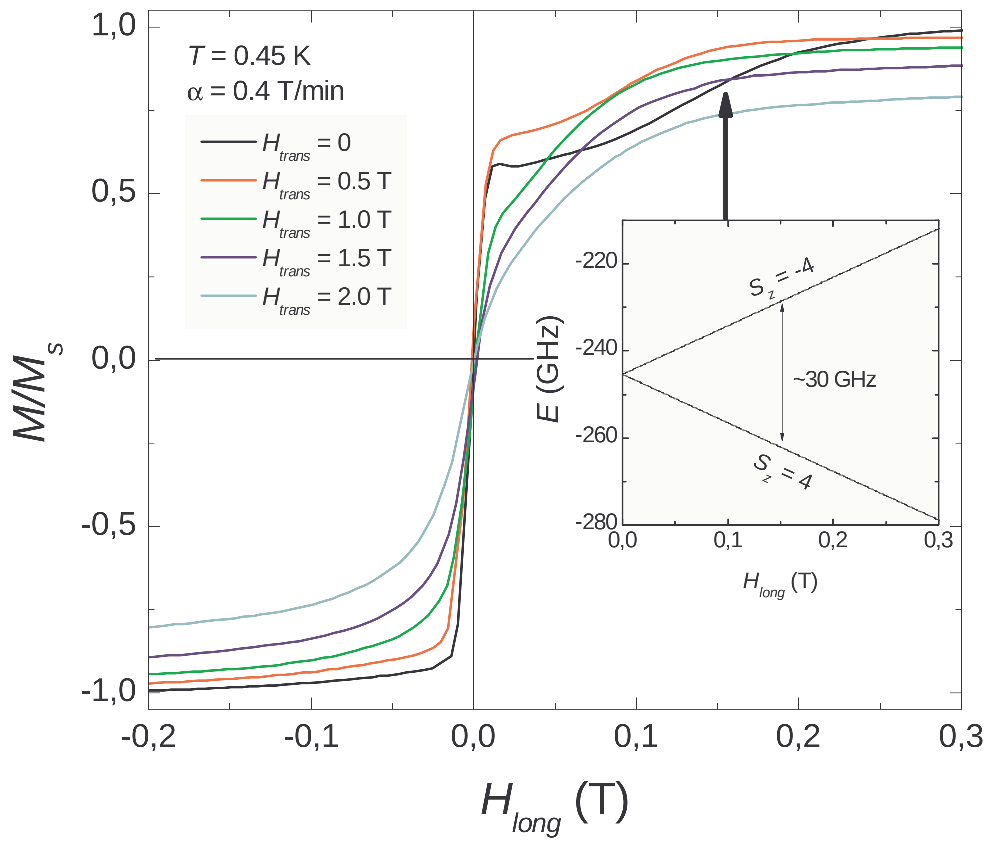

FIG. 1: Magnetization curves of Ni_4 obtained sweeping at a constant rate, $\alpha = 0.4$ T/min, a longitudinal magnetic field in the presence of different transverse fields. The inset shows the energy of the lowest levels as a function of the longitudinal field.

tometers cannot be used in ultra-fast time resolved measurements ($\sim$ 10 GHz), after all, the same semiconductor heterostructure materials used for Hall-magnetometers are used in high-speed circuitry. We note that time resolved magnetic measurements at the nanosecond time scale with micro-SQUIDs have not yet been demonstrated, only fast measurements with SQUIDs specialized for another purpose [15]. The main advantage of Hall magnetometry is the possibility of high sensitivity magnetic measurements over a the wide range of temperatures and applied fields (including, very large applied fields).

As alluded to in the Comment, spin-phonon relaxation processes are poorly understood in SMMs (see, for example, ref. [16]). It is certainly true that a spin-phonon-bottleneck can affect the relaxation time in SMMs [18] . We considered this possibility. The small phonon heat capacity and small coupling of sample phonons to the (cryostat) environment can create

an out-of-equilibrium distribution of phonons [19]. We have observed this phenomenon in our Ni_4 experiments (not reported in ref. [2]) as a plateau in the magnetization hysteresis curve (magnetization lower than its saturation value) after sweeping thought zero field (resonance $k = 0$) in the absence of transverse fields (see fig. 1) [17]. The magnetization approaches its equilibrium value when the longitudinal field is ~ 0.15 T. At this field the separation between lowest levels is about 30 GHz (see inset in fig. 1). At this frequency, the density of available phonon modes is apparently sufficient to allow energy relaxation on the time scale of the hysteresis sweep. Importantly, this plateau gradually disappears with increasing magnitude of an applied transverse field. This is due to the fact that a transverse field increases the energy splitting at the resonance, allowing the system to reach a state in which more and more phonons become available (the distribution of thermal phonons reaches a maximum at $3k_BT/h \sim 20 - 40$ GHz).

It is clear from this line of reasoning that since the density of phonon modes increases with frequency ($\sim \omega^2$), the effective relaxation time for a process limited by the phonon-bottleneck should *decrease* with increasing radiation frequency ($\tau \sim 1/\omega^2$). However, in our experiments with pulsed microwave fields we observe the opposite behavior (see Fig. 3C of Ref. [2]), which is not understood. Therefore, and as claimed in Ref. [2], the observed dependence of the relaxation time on frequency is opposite that expected based on the increasing phase space available for phonon generation.

On the last point, we note that our experiments with microwave radiation in Ni_4 have been carried out in the presence of transverse fields. For this reason, our experiments [2] differ significantly from those discussed above [3, 7]. A magnetic field applied perpendicular to the uniaxial anisotropy axis of the molecules breaks the degeneracy between symmetric and antisymmetric superpositions of S_z spin projections, producing an energy splitting between the states, known as the tunnel splitting. We note that in Refs. [3, 7] the energy splitting between states is linear with applied field and simply corresponds to the Zeeman splittings between S_z states. The tunnel splittings are not directly resolved in these experiments. In our experiments these splittings are directly resolved and reflect the formation of high spin-superposition states. The lower bound on the coherence time has been determined for these states to be ~ 1 ns, an order of magnitude higher than the time scale set by radiation frequency used in the experiment. The observation of quantum coherence between high spin-states clearly motivates future work in our group and others that will examine the

quantum dynamics in the frequency and time domain, such as Rabi experiments.

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[1] W. Wernsdorfer, arXiv:cond-mat/0405501 (2004).

[2] E. del Barco, A. D. Kent, E. C. Yang and D. Hendrikson, arXiv:cond-mat/0405331 (2004).

[3] W. Wernsdorfer *et al*, arXiv:cond-mat/0404410 (2004).

[4] A superconducting vector magnet and a high frequency vector network analyzer were purchased mainly for this purpose. At this time the plan to do this experiment at NYU was presented at a meeting in London in May 2002 to several collaborators and Wernsdorfer was present at this meeting .

[5] E. del Barco, "Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni_4", (invited talk), APS March Meeting - Montreal, (2004). Wernsdorfer also presented an invited talk in this session.

[6] A. D. Kent, "Magnetic Quantum Tunneling and Coherence in Single Molecule Magnets," 2004 Winter Conference on Condensed Matter Physics, Spins in Nanostructures, January 4-11, (2004).

[7] M. Bal *et al*, arXiv:cond-mat/0404448(2004).

[8] E. del Barco *et al.*, Europhys. Lett. **47**, 722 (1999).

[9] see, also, S. Hill, R. S. Edwards, N. Aliaga-Alcalde and G. Christou, Science **302**, 1015 (2003) and references therein.

[10] R. Amigo *et al*, Phys. Rev. B**67**, 220402 (2003).

[11] L. Sorace *et al*, Phys. Rev. Lett. **68**, 220407 (2003).

[12] C. H. van der Val *et al.*, Science **290**, 773 (2000).

[13] J. R. Friedman *et al.*, Nature **406**, 43 (2000).

[14] Y. Q. Li, P. Xiong, S. von Molnar, S. Wirth, Y. Ohno and H. Ohno, "Hall magnetometry on a single iron nanoparticle," Appl. Phys. Lett. **80**, 4644 (2002).

[15] I. Chiorescu *et al.*, Science **299**, 1869 (2003).

[16] E. M. Chudnovsky, Phys. Rev. Lett. **92**, 120405 (2004).

[17] also, Wernsdorfer *et al.* private communication and various conference presentations (2002).

[18] I. Chiorescu *et al.*, Phys. Rev. Lett. **84**, 3454 (2000).

[19] A. Abragam and B. Bleaney, *Electron paramagnetic resonance of transition ions* (Clarendon Press, Oxford, 1970).